

Structures and Properties of Supramolecular Assembled Fullerenol/Poly(dimethylsiloxane) Nanocomposites

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We prepared supramolecular assembled fullerenol/poly (dimethylsiloxane) nanocomposites by solution-casting the complexes of fullerenol and poly (dimethylsiloxane) (PDMS-di-NH₂) at different molar ratios. The results from our small-angle x-ray scattering (SAXS) study of the nanocomposites indicate that nanodomains of fullerenol aggregates are confined homogeneously in the PDMS matrix and grow in size when fullerenol molecules are gradually added. This novel structural feature, together with the unique molecular properties of fullerenol, gives these nanocomposites superior thermal and thermal mechanical stability, excellent elastic response, and attractive dielectric properties — i.e., one can enhance the permittivity but dramatically decrease the loss factor of the materials.

Fullerene-based nanomaterials are popular research targets due to their unique electrical and optical properties. However, the low solubility of fullerenes in polar media and the difficulty of controlling their aggregation states have prevented these materials from being fabricated into novel materials for advanced applications. One strategy for overcoming these obstacles is to modify fullerenes, such as C₆₀, and incorporate them into polymer matrixes. Poly(dimethylsiloxane) (PDMS-di-NH₂) is an ideal polymer candidate to host C₆₀ due to its many useful properties, such as its flexibility, low glass transition temperature, very low surface energy, good thermal stability, and biocompatibility. Making novel materials that combine the outstanding properties of C₆₀ fullerene and PDMS is thus desirable.

Recently, we prepared a series of freestanding C₆₀-containing PDMS nanocomposite films via the strong hydrogen bonding interactions between the hydroxyl (-OH) groups of fullerenol and the terminal NH₂ groups of PDMS. **Figure 1** shows the small-angle x-ray scattering (SAXS) profiles of pure PDMS-di-NH₂ and the fullerenol/PDMS nanocomposite films formed at different molar ratios of OH/NH₂. While the bulk PDMS-di-NH₂ has no scattering peaks, the fullerenol/PDMS composites exhibit a single scattering peak, as a result of the homogeneous embedding of fullerenol domains in the PDMS matrix. The gradual addition of fullerenol into the nanocomposites not only sharpens and intensifies the peaks, but also shifts the peak positions to lower *q* values, indicating a gradual increase in the inter-distances of fullerenol nanodomains. In our design, the fullerenol molecules are constrained by the end-functionalized PDMS chains, which means that the distance between neighboring fullerenol nanodomain surfaces should be equivalent to the PDMS chain length. Therefore, the increase in the inter-distances of fullerenol nanodomains could only be explained by an increase in the size of individual fullerenol nanodomains.



Figure 2 depicts the formation and expansion process of fullerenol nanodomains in fullerenol/PDMS

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nanocomposites upon a gradual addition of fullereneol molecules. This three-dimensional network structure, with fullereneol nanodomains homogeneously confined in the PDMS matrix, gives the material superior thermal and thermal mechanical stability, a strongly suppressed crystalline phase, and excellent elastic mechanical properties. More importantly, the controllable size of these fullereneol nanodomains enables us to adjust the dielectric constants of the nanocomposite films. **Figure 3** shows the temperature dependence of dielectric permittivity (ϵ') and loss factor (ϵ'') of PDMS-di-NH₂ and the fullereneol/PDMS composite film, formed at a molar ratio of OH/NH₂ = 2:1 under several frequencies. The strong interactions between fullereneol and PDMS-di-NH₂ can severely restrain the dipole mobility, resulting in very low ϵ' and ϵ'' values. On the other hand, the unrestricted, highly polar fullereneol molecules possess very high ϵ' values due to their direct current conductivity. For relatively large fullereneol nanodomains, only those OH groups located on the domain surface were linked with the PDMS chains. Thus, the unrestricted interior fullereneol molecules could enhance the ϵ' value for the nanocomposites, which explains the higher ϵ' value of the nanocomposite film than that of PDMS-di-NH₂ (**Figure 3A**). This unique dielectric property of Fol/PDMS-di-NH₂ nanocomposites has the potential to lead to novel materials with high ϵ' values and much lower ϵ'' values.

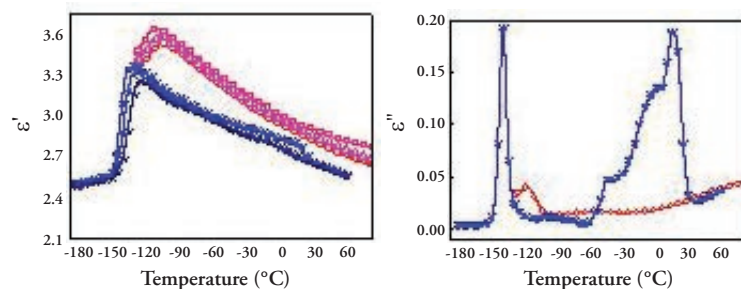


Figure 3. Temperature dependence of ϵ' and ϵ'' of PDMS-di-NH₂ (star symbols) and fullereneol/PDMS composite film formed at a molar ratio of OH/NH₂ = 2:1 (solid symbols). ϵ' = 0.3 kHz (square), 3 kHz (up triangle), and 30 kHz (circle). ϵ'' = 0.3 kHz.

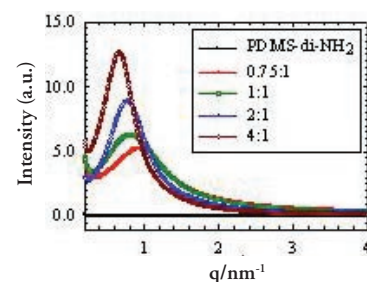


Figure 1. SAXS profiles of pure PDMS-di-NH₂ and fullereneol/PDMS nanocomposite films formed at different molar ratios of OH/NH₂ groups.

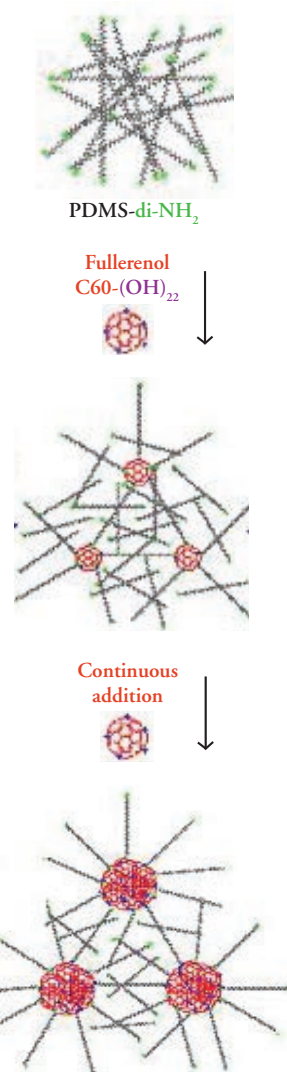


Figure 2. Structural model for the formation of fullereneol/PDMS nanocomposites and the expansion of fullereneol nanodomains upon the continuous addition of fullereneol molecules.